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Non-uniform polonium distribution in lead–bismuth eutectic revealed by evaporation experiments

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Abstract Understanding polonium evaporation from lead-bismuth eutectic (LBE) is required for the design of nuclear installations that use liquid LBE as coolant or spallation target. In the present study we measured the time-dependent release of polonium from LBE samples in Ar/5 %H_2 and Ar between room temperature and 500 °C. Our experiments revealed that the majority of polonium in the samples evaporated according to established temperature correlations for the Henry constant of polonium in LBE. However a small fraction of polonium in the LBE behaved differently, causing a relatively large but transient polonium release at the start of evaporation experiments. We showed that this volatile fraction of polonium was located near the sample surface and was formed after prolonged exposure of the samples to air at room temperature. We speculate that the peculiar evaporation behavior of this surface polonium is caused by enrichment and association with an oxide layer.

Keywords Lead–bismuth eutectic · LBE · Liquid metal · Evaporation · Polonium · MYRRHA

Introduction

Lead–bismuth eutectic (LBE, 44.5 wt% Pb; 55.5 wt% Bi) is a promising candidate spallation target material and coolant for innovative spallation neutron sources and accelerator driven systems (ADS) [1, 2]. A concern with the use of LBE is that large quantities of ^{210}Po are formed by activation of Bi in the coolant. When ^{210}Po, a pure alpha emitter, is released from LBE, it presents a challenge to the safety of the nuclear facility. Evaporation is considered an important release mechanism for polonium, but is relatively poorly understood. Quantitative understanding of the chemical processes governing polonium evaporation is essential for safety evaluations and for the development of technology for polonium capture and decontamination [3–5]. Under the impetus of the Multi-purpose hYbrid Research Reactor for High-tech Applications (MYRRHA) project [2], an LBE-based ADS, polonium evaporation from LBE is currently investigated by a combined experimental [6–8] and theoretical [9] approach.

During the last decade it was found that at high temperature between ca. 600 °C and 1,000 °C, polonium evaporates quite reproducibly from LBE, and appears insensitive to the presence of hydrogen in otherwise inert cover gas. Henry's law constants of Po in LBE in this temperature range have been independently determined by several research groups including our own [8, 10–13]. The Henry's law constants at these high temperatures are well described by an Antoine-type relation which we will denote as "high-temperature correlation" in the remainder of this work. The high-temperature correlation derived

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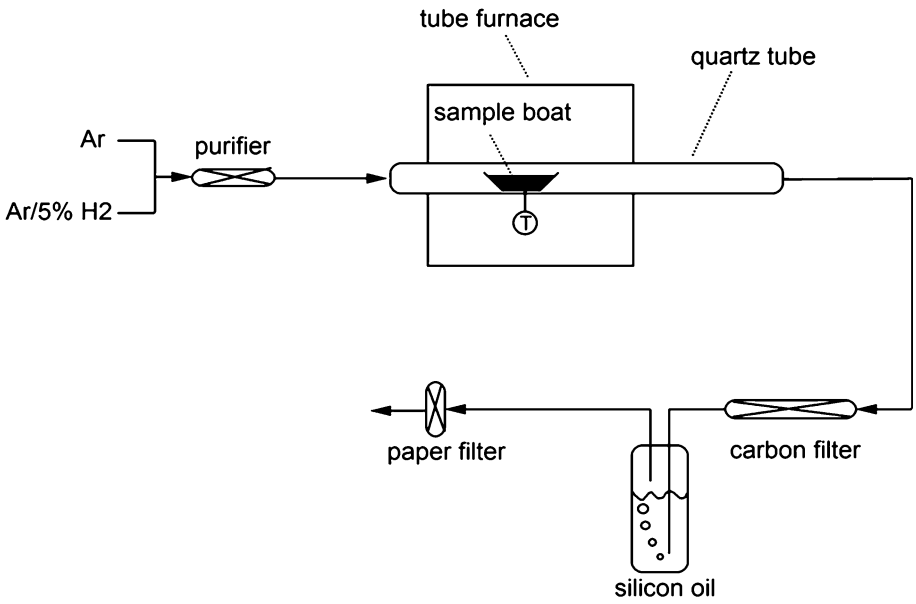

Fig. 1 Transpiration setup used for evaporation experiments

from measurements between 700 and 1,000 °C in Ar/5 %H_2 is

$$K_{\mathrm{Po(lbe)}} = 10^{(A+B/T)} \quad (1)$$

with coefficients $A = 10.7$ and $B = -8{,}516$ [8].

Recently, however, in a series of dynamic transpiration-type evaporation experiments at low temperatures, significant deviations from this evaporation regime were found [6]. Between 164 and 500 °C in inert gas Po evaporation was much higher than expected from the high-temperature correlation. These results in inert gas and especially results from comparable experiments in H_2 [6] were reminiscent of the increased polonium evaporation between 195 and 550 °C in static evaporation experiments in Ar/H_2/H_2O atmosphere [10]. This observation was originally attributed to the formation of H_2Po [10], but this assignment has been questioned [14].

These observations of increased polonium volatility at temperatures under which LBE-based facilities have operated [15] or are foreseen to operate [2] are of particular interest for the safety and licensing of such installations.

We here report the results of a series of experiments in which the release of polonium from LBE below 600 °C was determined at different evaporation times. The results offer a phenomenological explanation for the increased evaporation in transpiration experiments at low temperatures.

Experimental

Samples of LBE (ca. 2.7 g) containing 10^{-10} mol fraction of polonium were obtained by neutron irradiation of LBE [8]. After irradiation, samples were stored for several months in air at ambient temperature (ca. 20 °C).

Evaporation experiments were performed in a transpiration setup described in detail elsewhere [8]. A schematic drawing of this setup is shown in Fig. 1. Briefly, the transpiration setup consisted of a quartz tube inserted in a tubular furnace. Carrier gas flows through the system were either Ar or Ar/5 %H_2. The Po-doped LBE sample was placed on a boat-shaped Mo foil in the center of the furnace.

For evaporation experiments samples were loaded in the quartz tube and the system was flushed with carrier gas. An experimental run was started by setting the gas flow rate to 15 mL min^{-1} at standard temperature ($T_0 = 0$ °C) and pressure (1 bar) (STP). The tubular furnace was preheated (25–500 °C) and was shifted to the sample position. The sample temperature was measured by a thermocouple positioned in the gas near the sample surface. Once the sample reached constant temperature, the gas flow rate was increased to the experimental value of $\dot{V} = 100$ mL min^{-1}. This marked the start of the experimental run. After heating the sample for a certain time, the oven was shifted off the sample position and the gas flow rate was again reduced. When the sample reached room temperature, the quartz tube was opened and the sample was removed. The amount of evaporated polonium was then quantified. The tube was rinsed with a 7 M HNO_3 (aq) solution to dissolve polonium that had condensed on the quartz tube walls. Rinsing was performed twice, to ensure that all Po was dissolved. A fraction of the rinsing volume was mixed with scintillation cocktail for activity measurement by liquid scintillation counting (see Ref. [8] for details). A gas washing bottle containing 0.1 N NaOH (aq) was installed downstream of the quartz tube. This NaOH (aq)

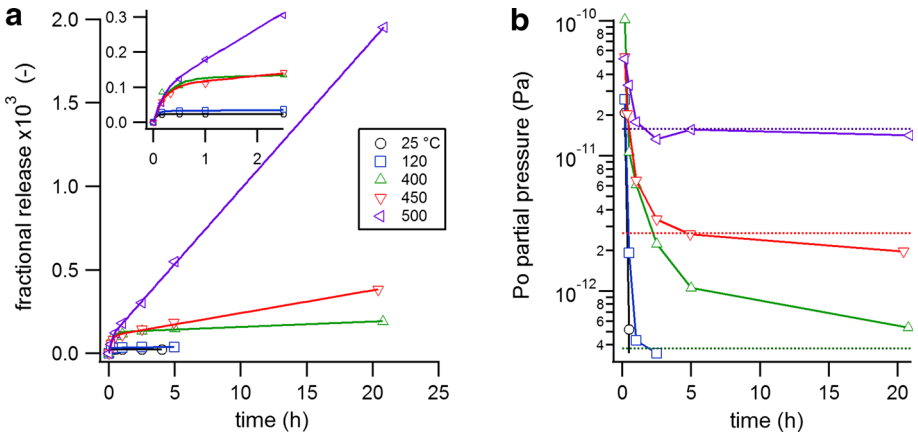

Fig. 2 **a** Fractional Po release from LBE after different heating times, at various temperatures. The *inset* is a magnification of the release at short heating times. Average standard error on the release data was 12 %. *Solid curves* are fits using Eq. (4). **b** Corresponding evolution of the partial pressures of ^{210}Po during each of the experiments. *Dotted horizontal lines* indicate the calculated partial pressures of Po according to the high-temperature correlation [Eq. (1)]

solution works as an efficient trap to collect Po species that are sufficiently volatile to be transported out of the quartz tube [10]. No polonium could be detected in the gas washing bottle installed containing the aqueous NaOH solution. It was thus verified that the condensate in the quartz tube contained all evaporated polonium.

This procedure was repeated and after each run the amount of released polonium was determined. The result was a set of measurements of the polonium release after different heating times. Between different runs, the samples were exposed to air for a short period of time (<5 min). This brief intermediate exposure did not change the release behavior (see below).

Results and discussion

The time dependent fractional release of Po from LBE samples showed a two-stage trend, at each of the studied temperatures under a 100 mL min^{-1} flow of Ar/5 %H_2 (Fig. 2a). Surprisingly, at experiment times less than 1 h (Fig. 2a, inset), Po release was fast and non-linear. At longer experiment times and at temperatures between 400 and 500 °C the release followed a linear trend. These long term trends were entirely in agreement with predictions using the high-temperature correlation [Eq. (1)] and the transpiration model for polonium evaporation which predicts linear behavior at low fractional release [8]. Remarkably, a small amount of Po release could even be measured in experiments with solid LBE at 25 and 120 °C. For these solid samples, measurable Po release only occurred during the first hours of the experiments.

The variation of the partial pressure of polonium in the gas p_{Po} flowing through the tube during the experiment was calculated from the fractional release data according to

$$p_{Po} = \frac{\Delta n_{Po(lbe)}}{\Delta t}\frac{RT_0}{\dot{V}} \quad (2)$$

where $\Delta n_{Po(lbe)}$ [mol] is the change of polonium content in the sample in time interval Δt and R is the ideal gas constant. During the first hours (Fig. 2b), the Po partial pressure decreased rapidly by a factor of ca. 100, before reaching almost constant values in agreement with predictions of the high-temperature correlation for the Henry constant of Po in LBE and the average polonium concentration in the sample (dotted lines in Fig. 2b). The Po partial pressure of solid samples rapidly dropped to levels below detection limit.

Similar trends were observed in experiments with pure Ar as carrier gas (Online Resource). The presence of 5 % hydrogen in the gas stream apparently did not enhance Po volatility during the experiment under these particular experimental conditions.

We explain these experimental trends, in a first approximation, by assuming the presence of two types of polonium in the sample, which evaporate independently. The first type of polonium is evaporated rapidly and completely during the first hours of the experiment. It represents only a small fraction of the total amount of polonium in the sample and causes high partial pressures. The second type represents the majority of the polonium in the sample. Its partial pressure is well described by the high-temperature correlation for the Henry constant of Po in LBE.

We further make the hypothesis that the small amount of fast-released polonium is concentrated at the surface of the sample. It is known that in solid LBE, polonium tends to enrich at the surface [16, 17], where it is probably associated with an oxide layer. Such an oxide layer enriched in polonium could be preserved upon LBE melting and float

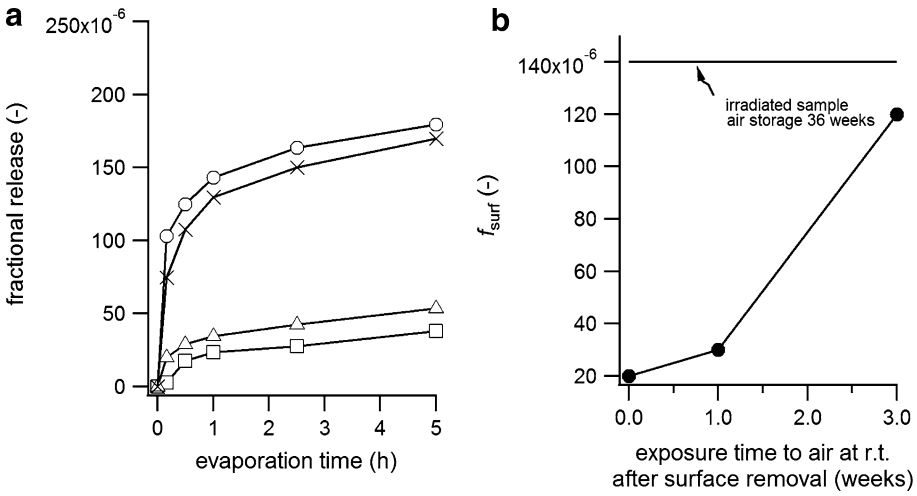

Fig. 3 **a** Polonium release in Ar/5 %H_2 at 400 °C after mechanical removal of the surface of an LBE sample and subsequent exposure of the bulk to air at room temperature for different times: *squares* immediately after removal, *triangles* 1 week exposure, *crosses* 3 weeks exposure and *circles* sample which was stored in air for 36 weeks without surface removed. **b** Evolution of the fraction of surface polonium f_{surf} with exposure time [see Eq. (4)]. *Horizontal line* sample without surface removed

on top of liquid LBE as in the current experiments, provided that the oxygen content in the sample is above the saturation limit at the experimental temperature [18].

To verify whether the initial polonium release was indeed associated with the surface, we mechanically removed by manual cutting about 1 mm of the surface layer of the LBE samples and did evaporation experiments using only the remaining bulk of the sample (Fig. 3). The result confirmed our hypothesis. The initial enhanced Po evaporation was reduced by a factor of ca. 10 when the surface was removed. There was still a small initial enhanced release, possibly because removal of the surface was not complete, but the trend was clearly dominated by the long-time evaporation. This experiment proved that the fast-released polonium was surface-related.

In solid LBE stored in air at room temperature, enrichment occurs on timescales of the order of days to weeks [17]. To investigate a possible connection between enrichment and Po evaporation, we verified if and on what timescale the fast-released, surface polonium was recovered after storing the bulk sample in air at room temperature. Exposure of samples for a few minutes to air did not restore the fraction of surface polonium. However it was found that the surface polonium did reappear on much longer time scales of weeks (Fig. 3a). After 3 weeks of exposure to air, the amount of surface polonium that was present before cutting off the surface, was almost completely restored.

We now present a quantitative analysis of the results by assuming that during evaporation experiments the total polonium in the sample $n_{Po(lbe)}$ is the sum of polonium in the bulk $n_{Po(lbe,b)}$ and that in the region close to the sample surface $n_{Po(lbe,s)}$:

$$n_{Po(lbe)}(t) = n_{Po(lbe,b)}(t) + n_{Po(lbe,s)}(t) \quad (3)$$

The decrease of the amount of each type of polonium with time during transpiration-type evaporation experiments is described by a first order model. We refer to the Online Resource and Ref. [8] for a derivation of that model. The sum of surface and bulk polonium remaining in the sample after evaporation time t is then given by:

$$n_{Po(lbe)}(t) = n_{Po(lbe,b)}(0)\exp\left(-\frac{K_{Po(lbe,b)}}{n_{lbe,b}}\frac{\dot{V}t}{RT_0}\right) + n_{Po(lbe,s)}(0)\exp\left(-\frac{K_{Po(lbe,s)}}{n_{lbe,s}}\frac{\dot{V}t}{RT_0}\right) \quad (4)$$

The evaporation equilibria of bulk and surface polonium are characterized by temperature dependent Henry constants $K_{Po(lbe,b)}$ and $K_{Po(lbe,s)}$, respectively. It is assumed that there is no significant conversion from one type of polonium into the other under the conditions of the evaporation experiments. The quantities $n_{lbe,b}$ and $n_{lbe,s}$ are those parts of the LBE sample [mol] in which bulk and surface polonium are respectively located, with $n_{lbe,b} + n_{lbe,s} = n_{lbe,tot}$. The total fractional polonium release as given in Figs. 2a and 3a is defined as $\phi_{tot}(t) = 1 - n_{Po(lbe)}(t)/n_{Po(lbe)}(0)$.

The experimental data could be quite satisfactorily simulated with the two-population model of Eq. (4) (solid curves in Fig. 2a). Here, the parameters $n_{lbe,tot}$ and $\dot{V}$ were fixed to their experimental values and it was assumed that $n_{lbe,b}$ was equal to the total amount of LBE in the sample. The latter implies that the surface polonium $n_{Po(lbe,s)}$ is concentrated in a comparatively very small part of the sample, i.e. $n_{lbe,s} \ll n_{lbe,b} \approx n_{lbe,tot}$. This assumption seemed reasonable because it was observed previously that in solid LBE samples polonium tended to be enriched only in the first few micrometers below the sample surface [17].

The other independent parameters of Eq. (4), $n_{Po(lbe,s)}(0)$, $K_{Po(lbe,b)}$, and the ratio $K_{Po(lbe,s)}/n_{lbe,s}$ were derived from the fit. From the fitted value of $n_{Po(lbe,s)}(0)$, we determined the fraction of surface polonium initially present in the LBE sample, defined as $f_{surf} = n_{Po(lbe,s)}(0)/n_{Po(lbe)}(0)$. This value

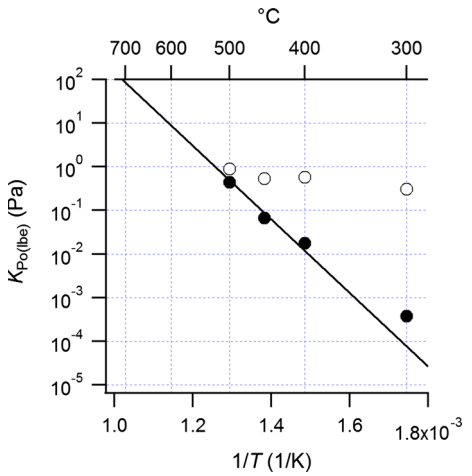

Fig. 4 Henry constants of Po in LBE obtained from release data by different analysis methods. *Filled circles* $K_{Po(lbe,b)}$ derived from analysis assuming two forms of Po (see text). *Open circles* analysis with assumption of only a single form of polonium. *Solid line* high-temperature correlation

corresponds to the intercept of the extrapolation of the long-term fractional release in Figs. 2a and 3a. In experiments with liquid LBE samples, the fraction of surface polonium f_{surf} was about 10^{-4} of total polonium in the sample. The change of f_{surf} after mechanical removal of the sample surface and after subsequent exposure of the bulk to air at room temperature is shown in Fig. 3b.

The fitted Henry constants of the bulk polonium, $K_{Po(lbe,b)}$, were in very good agreement with the high-temperature correlation given by Eq. (1) (Fig. 4). Up to now the lowest temperature reported in literature where the high-temperature correlation was found to be valid was about 400 °C [10]. With the current results we provide evidence that the high-temperature correlation holds to temperatures down to 300 °C for Po in bulk LBE which represents the majority of the Po in the LBE sample. To allow accurate measurement of long-term polonium evaporation at a temperature as low as 300 °C, surface polonium was first removed by pretreatment at 400 °C for 20 h in Ar/5 %H_2.

In previous work [8, 11, 13], fractional polonium release data were analyzed assuming one, uniformly distributed type of polonium only, instead of the two types of polonium discovered in the present work. Below 500 °C, Henry constants calculated from release data considering just one type of polonium can be orders of magnitude larger than predicted by the high-temperature correlation of Eq. (1). This is shown in Fig. 4. Likewise, the presence of two types of polonium, or, in more general terms, two polonium release mechanisms, could offer an explanation for the high values of the Henry constants reported by Rizzi et al. [6], which were derived with the assumption of one type of polonium only.

Unfortunately, with the two-population model it was not possible to determine the Henry constant of the surface polonium $K_{Po(lbe,s)}$, which would be a measure of its equilibrium volatility. Although $K_{Po(lbe,s)}$ appears in Eq. (4), its value cannot be determined independently from $n_{lbe,s}$. With the current experiments we can only ascertain that the surface polonium gives rise to high partial pressures (Fig. 2b). Surface polonium is likely present in a chemical state that is more susceptible to volatilization than polonium in the bulk. The association of Po with a thin Pb/Bi oxide layer located at the surface, and reactions occurring with traces of water vapor in the carrier gas [7] may enhance the effective volatility of surface polonium.

It has been suggested based on thermochromatography experiments that at high temperature under both inert and reducing conditions, Po evaporates as elemental Po(g), or as BiPo(g) in case it was produced by irradiation of bismuth [7]. In samples containing lead such as LBE, evaporation as PbPo(g) is also possible. The present experiments show that at low temperatures (<600 °C) bulk polonium has a Henry constant which is in agreement with the high-temperature evaporation behavior. It is therefore logical to assume that bulk polonium evaporated at low temperature has the same chemical form as that encountered in experiments at higher temperature i.e. elemental polonium or metal polonide with Bi or Pb.

The chemical nature of the volatile species that is formed during evaporation of surface polonium is currently unknown. However, formation of a very volatile species like H_2Po seemed unlikely for two reasons. First, in experiments with Ar/5 %H_2 as carrier gas we did not detect any polonium in the aqueous NaOH solution downstream of the evaporation tube (see Sect. 2). H_2Po has an estimated boiling point at atmospheric pressure of 37 °C [19, 20] and therefore should have been easily transported to the NaOH trap. Secondly, also in absence of H_2 in the carrier gas, the fast-released surface polonium was detected (see Online Resource). This seems to exclude the possibility of H_2Po as the dominant vapor species. Formally, in absence of H_2, water vapor impurities could act as hydrogen donor to form H_2Po from PbPo, but this reaction is thermodynamically unfavorable [21]. On the other hand, the presence of water vapor in the carrier gas, even in trace amounts, has been found to produce relatively volatile polonium species, which were tentatively identified as polonium hydroxides or oxyhydroxides [7]. Such species are plausible candidates for the evaporated surface polonium molecules.

Conclusions

Evaporation experiments in Ar/5 %H_2 and Ar revealed that polonium in LBE samples existed in two forms. A small

fraction of polonium was located near the sample surface. This surface polonium had a high volatility and was quickly depleted during evaporation experiments. Surface polonium was formed during exposure of LBE samples to air at room temperature for several weeks. The majority of polonium (about 99.99 %) however was located in the bulk of the LBE samples and evaporated according to previously established high-temperature correlations.

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